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**The attached documents are a correct and accurate reproduction of the original submission for this Application.**

Munich, 15 October 2001

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**Tetrakisfluoroalkylborate salts and their**  
**use as conducting salts**

## Tetrakisfluoroalkylborate salts and their use as conducting salts

The present invention relates to tetrakisfluoroalkylborate salts, methods of producing same, and their use in electrolytes, batteries, capacitors, supercapacitors, and galvanic cells.

In recent years, the spreading of portable electronic devices such as laptop and palmtop computers, cell telephones, or video cameras and thus, the demand for light-weight and high-performance batteries has dramatically increased worldwide.

In view of such rapidly increasing demand for batteries and the associated ecological problems, the development of rechargeable batteries having long service life has become more and more important.

Starting in the early nineties, rechargeable lithium ion batteries have been traded commercially. Most of these batteries work with lithium hexafluorophosphate as conducting salt. However, this lithium salt is a compound which is extremely sensitive to hydrolysis and has low thermal stability and therefore, due to such properties of this salt, appropriate lithium batteries can only be produced by means of very inconvenient and thus also very cost-intensive processes. Also, the sensitivity of this lithium salt reduces the service life and the performance of such lithium batteries, impairing their use under extreme conditions, such as high temperatures.

Therefore, numerous attempts have been made to provide lithium salts having improved properties. Thus, U.S. Pat. No. 4,505,997 and U.S. Pat. No. 9,202,966 describe the use of lithium [bis(trifluoromethylsulfonyl)imide] or lithium [tris(trifluoromethylsulfonyl)methanide] salts as conducting salts in batteries. Both of these salts have high anodic stability, forming solutions of high conductivity with organic carbonates. However, lithium bis(trifluoromethylsulfonyl)imide has the drawback of insufficient passivation of the aluminum metal functioning as cathodic current conductor in lithium batteries. On the other hand, the production and purification of lithium tris(trifluoromethylsulfonyl)methanide is only possible with exceedingly high efforts, so that the use of this salt as conducting salt in batteries massively increases the production cost of such lithium batteries.

Another lithium salt used in battery cells is lithium tetrafluoroborate. However, this salt has a relatively low solubility in most solvents, so that solutions thereof generally have low ionic conductivities.

5

It is therefore the object of the present invention to provide conducting salts that would exhibit no or only slight evidence of hydrolytic decomposition over a long period of time. Furthermore, these conducting salts also should have high ionic conductivity, high thermal stability and from good to very good solubility in usual solvents. Another object of the present invention is to improve or enhance the service life and performance of primary and secondary batteries, capacitors, supercapacitors and/or galvanic cells.

Said object is accomplished by providing tetrakisfluoroalkylborate salts of general formula (I)

15



wherein

20

$M^{n+}$  is a univalent, bivalent, or trivalent cation, each of the ligands R are the same and represent  $(C_xF_{2x+1})$ , with  $1 \leq x \leq 8$ , and  $n = 1, 2$  or  $3$ .

Preferred are those tetrakisfluoroalkylborate salts of the invention having the general formula (I), wherein the  $M^{n+}$  cation is an alkali metal cation, preferably a lithium, sodium or potassium cation, and more preferably a lithium cation, a magnesium or aluminum cation.

25

Furthermore, those tetrakisfluoroalkylborate salts of general formula (I) are preferred wherein the  $M^{n+}$  cation is an organic cation, preferably a nitrosyl cation, a nitril cation, or a cation of general formula  $[N(R^7)_4]^+$ ,  $[P(R^7)_4]^+$ ,  $[P(N(R^7)_2)_4]^+$  or  $[C(N(R^7)_2)_3]^+$ , wherein each of the radicals  $R^7$  are the same or different, representing

30

35 H,

$C_oF_{2o+1-p-q}H_pA_q$ , or

A,

wherein

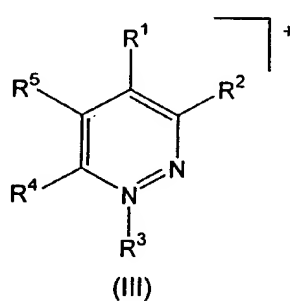
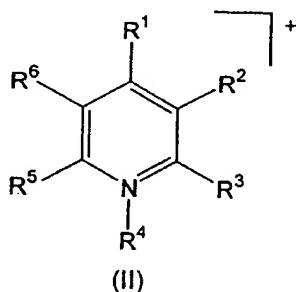
- 1  $1 \leq o \leq 10$ ,  $0 \leq p \leq 2o+1$ ,  $0 \leq q \leq 2o+1$ , preferably  $1 \leq o \leq 6$ ,  $0 \leq p \leq 2o+1$ ,  
 5 and  $0 \leq q \leq 2o+1$ , and A represents an aromatic radical optionally having heteroatoms, or a preferably 5- or 6-membered cycloalkyl radical.

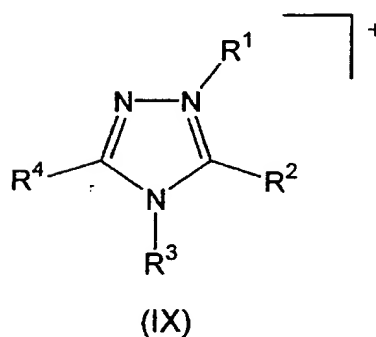
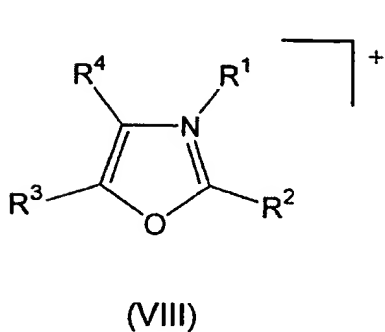
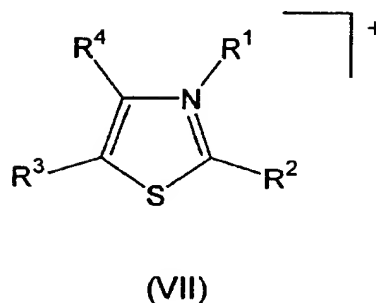
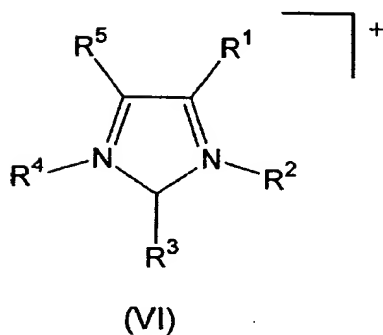
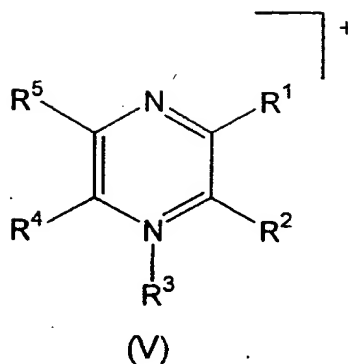
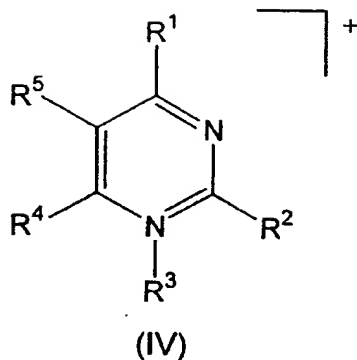
- All of the aromatic, heteroaromatic or cycloaliphatic compounds well-known to those skilled in the art and suitable in the preparation of  $[N(R^7)_4]^+$ ,  
 10  $[P(R^7)_4]^+$ ,  $[P(N(R^7)_2)_4]^+$  or  $[C(N(R^7)_2)_3]^+$  cations can be used as aromatic or cycloaliphatic radical A optionally including heteroatoms.

- Preferably, A represents a 5- or 6-membered aromatic radical optionally including nitrogen and/or sulfur and/or oxygen atoms, more preferably a  
 15 phenyl or pyridine radical.

- In another preferred embodiment of the present invention, the cation  $M^{n+}$  is a heteroaromatic cation selected from the group of heteroaromatic cations of general formulas (II) to (IX):

20





- The radicals  $R^1$  to  $R^6$ , each of which may be the same or different, represent an H, a halogen, preferably fluorine, or a  $C_{1-8}$  alkyl radical optionally substituted by F, Cl,  $N(C_aF_{(2a+1-b)}H_b)_2$ ,  $O(C_aF_{(2a-1-b)}H_b)$ ,  $SO_2(C_aF_{(2a+1-b)}H_b)$ , or  $C_aF_{(2a-1-b)}H_b$  substituents wherein  $1 \leq a \leq 6$ , and  $0 \leq b \leq 13$ . Likewise, two of the radicals  $R^1$  to  $R^6$  together may represent a  $C_{1-8}$  alkyl radical optionally substituted by F, Cl,  $N(C_aF_{(2a+1-b)}H_b)_2$ ,  $O(C_aF_{(2a-1-b)}H_b)$ ,  $SO_2(C_aF_{(2a+1-b)}H_b)$ , or  $C_aF_{(2a-1-b)}H_b$  substituents wherein  $1 \leq a \leq 6$ , and  $0 \leq b \leq 13$ .

Also preferred are tetrakisfluoroalkylborate salts of general formula (I) wherein each of the ligands R are the same, representing  $(C_xF_{2x+1})$ , and  $x = 1$  or  $2$ . Those tetrakisfluoroalkylborate salts are particularly preferred wherein each of the ligands R are the same, representing a  $CF_3$  radical.

The salts of the invention having the general formula (I) can be used both in pure form and in the form of mixtures thereof as conducting salts in electrolytes, primary and secondary batteries, capacitors, supercapacitors and/or galvanic cells. As conducting salts, it is also possible to use the salts according to the invention in mixture with other lithium salts well-known to those skilled in the art.

They can be used in amounts of between 1 and 99% in combination with other conducting salts that find use in electrochemical cells. For example, conducting salts selected from the group of  $LiPF_6$ ,  $LiBF_4$ ,  $LiClO_4$ ,  $LiAsF_6$ ,  $LiCF_3SO_3$ ,  $LiN(CF_3SO_2)_2$  or  $LiC(CF_3SO_2)_3$  and mixtures thereof are suitable.

The salts of formula (I) and mixtures thereof can also be used in electrolytes for electrochemical cells.

The electrolytes may also include organic isocyanates (DE 199 44 603) to reduce the water content.

Compounds of general formula



wherein

Kt represents N, P, As, Sb, S, Se,

A represents N, P, P(O), O, S, S(O),  $SO_2$ , As, As(O), Sb, Sb(O),

$R^1$ ,  $R^2$  and  $R^3$ , same or different, represent H, halogen, substituted and/or unsubstituted alkyl  $C_nH_{2n+1}$ , substituted and/or unsubstituted alkenyl having 1-18 carbon atoms and one or more double bonds, substituted and/or unsubstituted alkynyl having 1-18 carbon atoms and one or more triple

bonds, substituted and/or unsubstituted cycloalkyl  $C_mH_{2m-1}$ , mono- or polysubstituted and/or unsubstituted phenyl, substituted and/or unsubstituted heteroaryl,

5 A may be included at different positions in  $R^1$ ,  $R^2$  and/or  $R^3$ .

Kt may be included in cyclic or heterocyclic rings;  
the groups bound to Kt may be the same or different,

10 with

n 1-18,

m 3-7,

k 0, 1-6,

15 l 1 or 2 if  $x = 1$ , and 1 if  $x = 0$ ,

x 0, 1,

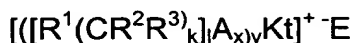
y 1-4,

may also be included (DE 99 41 566). The method of preparing these  
20 compounds is characterized in that an alkali salt of general formula



with  $D^+$  selected from the group of alkali metals, is reacted in a polar  
organic solvent with a salt of general formula

25

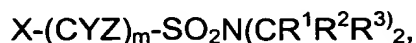


wherein

30 Kt, A,  $R^1$ ,  $R^2$ ,  $R^3$ , k, l, x, and y have the above-stated meanings, and

$E^-$  represents  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $BF_4^-$ ,  $ClO_4^-$ ,  $AsF_6^-$ ,  $SbF_6^-$ , or  $PF_6^-$ .

The compounds according to the invention may also be included in  
35 electrolytes comprising compounds of formula



with

X H, F, Cl,  $C_nF_{2n+1}$ ,  $C_nF_{2n-1}$ ,  $(SO_2)_kN(CR^1R^2R^3)_2$ ,

Y H, F, Cl,

Z H, F, Cl

5  $R^1, R^2, R^3$  H and/or alkyl, fluoroalkyl, cycloalkyl,

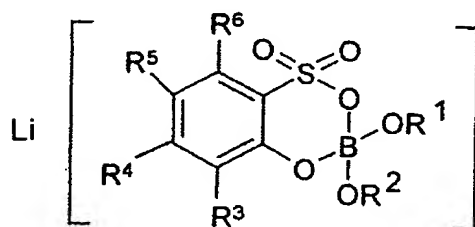
m 0-9, and if X = H,  $m \neq 0$ ,

n 1-9,

k 0 if  $m = 0$ , and  $k = 1$  if  $m = 1-9$ ,

10 prepared by reacting partially fluorinated or perfluorinated alkylsulfonyl fluorides with dimethylamine in organic solvents (DE 199 46 673).

Lithium complex salts of formula



15

wherein

$R^1$  and  $R^2$  are the same or different, optionally bound directly to each other by a single or double bond, each one alone or together representing an aromatic ring from the group of phenyl, naphthyl, anthracyl or phenanthryl, which may be unsubstituted or from mono- to hexasubstituted by alkyl ( $C_1-C_6$ ), alkoxy groups ( $C_1-C_6$ ), or halogen (F, Cl, Br), or

25 each one alone or together representing an aromatic heterocyclic ring from the group of pyridyl, pyrazyl or pyrimidyl, which may be unsubstituted or from mono- to tetrasubstituted by alkyl ( $C_1-C_6$ ), alkoxy groups ( $C_1-C_6$ ), or halogen (F, Cl, Br), or

30 each one alone or together representing an aromatic ring from the group of hydroxybenzenecarboxyl, hydroxynaphthalenecarboxyl, hydroxybenzenesulfonyl, and hydroxynaphthalenesulfonyl, which may be unsubstituted or from mono- to tetrasubstituted by alkyl ( $C_1-C_6$ ), alkoxy groups ( $C_1-C_6$ ), or halogen (F, Cl, Br),

R<sup>3</sup> to R<sup>6</sup>, each one alone or in pairs, optionally bound directly to each other by a single or double bond, may represent the following:

5 1. alkyl (C<sub>1</sub>-C<sub>6</sub>), alkoxy (C<sub>1</sub>-C<sub>6</sub>), or halogen (F, Cl, Br),

2. an aromatic ring from the groups of

10 phenyl, naphthyl, anthracyl, or phenanthryl, which may be unsubstituted or from mono- to hexasubstituted by alkyl (C<sub>1</sub>-C<sub>6</sub>), alkoxy groups (C<sub>1</sub>-C<sub>6</sub>), or halogen (F, Cl, Br),

15 pyridyl, pyrazyl or pyrimidyl, which may be unsubstituted or from mono- to tetrasubstituted by alkyl (C<sub>1</sub>-C<sub>6</sub>), alkoxy groups (C<sub>1</sub>-C<sub>6</sub>), or halogen (F, Cl, Br), prepared using the following method (DE 199 32 317)

a) 3-, 4-, 5-, 6-substituted phenol in a suitable solvent is added with chlorosulfonic acid,

20 b) the intermediate from a) is reacted with chlorotrimethylsilane, filtrated and subjected to fractionated distillation,

25 c) the intermediate from b) is reacted with lithium borate tetramethanolate (1-) in a suitable solvent, and the final product is isolated therefrom,

may be included in the electrolyte.

Electrolytes having complex salts of general formula (DE 199 51 804)

30



wherein

35 x, y represent 1, 2, 3, 4, 5, 6,

M<sup>x+</sup> represents a metal ion,

E represents a Lewis acid selected from the group of

$BR^1R^2R^3$ ,  $AlR^1R^2R^3$ ,  $PR^1R^2R^3R^4R^5$ ,  $AsR^1R^2R^3R^4R^5$ ,  $VR^1R^2R^3R^4R^5$ .

5  $R^1$  to  $R^5$ , same or different, optionally bound directly to each other by a single or double bond, each one alone or together may represent a halogen (F, Cl, Br),

10 an alkyl or alkoxy radical ( $C_1$ - $C_8$ ) which may be partially or completely substituted by F, Cl, Br,

an aromatic ring from the group of phenyl, naphthyl, anthracyl, or phenanthryl, optionally bound via oxygen, which may be unsubstituted or from mono- to hexasubstituted by alkyl ( $C_1$ - $C_8$ ) or F, Cl, Br,

15 an aromatic heterocyclic ring from the group of pyridyl, pyrazyl or pyrimidyl, optionally bound via oxygen, which may be unsubstituted or from mono- to tetrasubstituted by alkyl ( $C_1$ - $C_8$ ) or F, Cl, Br, and

20 Z represents  $OR^6$ ,  $NR^6R^7$ ,  $CR^6R^7R^8$ ,  $OSO_2R^6$ ,  $N(SO_2R^6)(SO_2R^7)$ ,  $C(SO_2R^6)(SO_2R^7)(SO_2R^8)$ ,  $OCOR^6$ ,

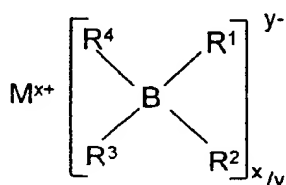
wherein

25  $R^6$  to  $R^8$  are the same or different, optionally bound directly to each other by a single or double bond, each one alone or together representing

hydrogen or having the meaning like  $R^1$  to  $R^5$ .

30 prepared by reacting an appropriate boron or phosphorus/Lewis acid/solvent adduct with a lithium or tetraalkylammonium imide, methanide or triflate, can also be used.

Borate salts (DE 199 59 722) of general formula



wherein

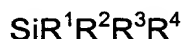
M represents a metal ion or a tetraalkylammonium ion,

5 x, y represent 1, 2, 3, 4, 5, or 6,

R<sup>1</sup> to R<sup>4</sup>, same or different, represent alkoxy or carboxy radicals (C<sub>1</sub>-C<sub>8</sub>) optionally bound directly to each other by a single or double bond, may also be included. These borate salts are prepared by reacting lithium borate tetraalcoholate or a 1:1 mixture of lithium alcoholate and a boric acid ester in an aprotic solvent with a suitable hydroxy or carboxy compound at a ratio of 2:1 or 4:1.

Additives such as silane compounds of general formula

15



with R<sup>1</sup> to R<sup>4</sup> H,

20 C<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>,

OC<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>,

OC(O)C<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>,

25

OSO<sub>2</sub>C<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>, and

1 ≤ x ≤ 6,

30 1 ≤ y ≤ 8, and

0 ≤ z ≤ 2y+1, and

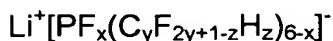
R<sup>1</sup>- R<sup>4</sup>, same or different, representing an aromatic ring from the group of phenyl, naphthyl, which may be unsubstituted or mono- or polysubstituted by F, C<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub> or OC<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>, OC(O)C<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>, OSO<sub>2</sub>C<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>, N(C<sub>n</sub>F<sub>2n+1-z</sub>H<sub>z</sub>)<sub>2</sub>, or representing a heterocyclic aromatic ring from the group of pyridyl, pyrazyl or pyrimidyl, each of which may be mono- or polysubstituted by F, C<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>, or OC<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>, OC(O)C<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>,

35

$\text{OSO}_2\text{C}_y\text{F}_{2y+1-z}\text{H}_z$ ,  $\text{N}(\text{C}_n\text{F}_{2n+1-z}\text{H}_z)_2$  (DE 100 27 626), may also be included.

The compounds according to the invention can also be used in electrolytes including lithium fluoroalkylphosphates of following formula

5



wherein

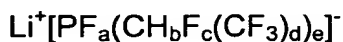
10  $1 \leq x \leq 5,$

$$3 \leq y \leq 8,$$

$$0 \leq z \leq 2y+1,$$

15

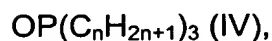
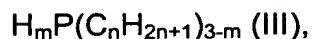
and the ligands  $(\text{C}_y\text{F}_{2y+1-z}\text{H}_z)$  may be the same or different, with compounds of general formula



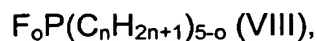
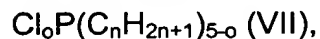
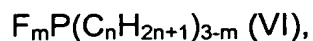
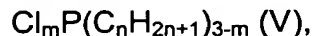
20

wherein a is an integer of from 2 to 5, b = 0 or 1, c = 0 or 1 d = 2, and e is an integer of from 1 to 4, with the proviso that b and c do not simultaneously represent zero, and the sum of a+e = 6, and the ligands  $(\text{CH}_b\text{F}_c(\text{CF}_3)_d)$  may be the same or different, being excluded (DE 100 08 955). The method of preparing lithium fluoroalkylphosphates is characterized in that at least one compound of general formula

25



30



35

wherein

$$0 < m < 2, 3 < n < 8, \text{ and } 0 < o < 4,$$

is fluorinated by electrolysis in hydrogen fluoride, the mixture of fluorination

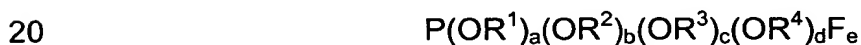
products thus obtained is separated by extraction, phase separation and/or distillation, and the fluorinated alkylphosphorane thus obtained is reacted in an aprotic solvent or mixture of solvents with lithium fluoride under exclusion of moisture, and the resulting salt is purified and isolated according to conventional methods.

The compounds according to the invention may also be used in electrolytes including salts of formula



wherein

15  $0 < a+b+c+d \leq 5$ , and  $a+b+c+d+e = 6$ , and  $\text{R}^1$  to  $\text{R}^4$  independently are alkyl, aryl or heteroaryl radicals, and at least two of  $\text{R}^1$  to  $\text{R}^4$  may be bound directly to each other by a single or double bond (DE 100 16 801). These compounds are prepared by reacting phosphorus(V) compounds of general formula



wherein

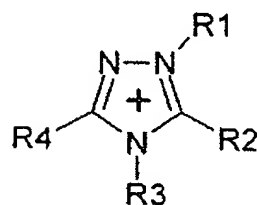
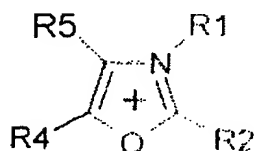
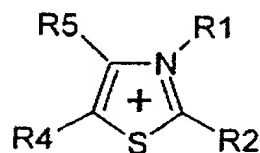
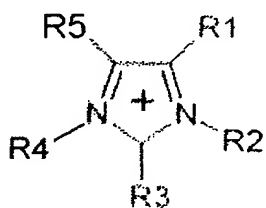
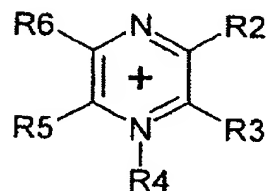
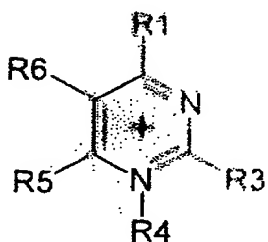
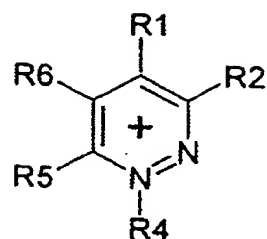
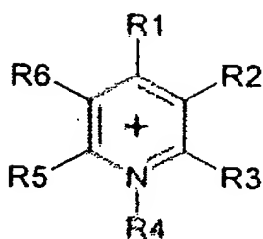
25  $0 < a+b+c+d \leq 5$ , and  $a+b+c+d+e = 5$ , and  $\text{R}^1$  to  $\text{R}^4$  have the above-stated meanings, with lithium fluoride in the presence of an organic solvent.

Ionic liquids of general formula



wherein

$\text{K}^+$  represents a cation selected from the group of



wherein

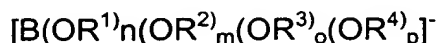
5  $R^1$  to  $R^5$  are the same or different, optionally bound directly to each other by a single or double bond, each one alone or together representing the following:

H,

10 halogen,

alkyl radical ( $C_1-C_8$ ) which may be partially or completely substituted by additional groups, preferably F, Cl,  $N(C_nF_{(2n+1-x)}H_x)_2$ ,  $O(C_nF_{(2n+1-x)}H_x)$ ,  $SO_2(C_nF_{(2n+1-x)}H_x)$ ,  $C_nF_{(2n+1-x)}H_x$ , with  $1 < n < 6$ , and  $0 < x \leq 13$ , and

A<sup>-</sup> represents an anion selected from the group of



5 with  $0 \leq n, m, o, p \leq 4$ , and

$$m+n+o+p = 4,$$

wherein

10

R<sup>1</sup> to R<sup>4</sup> are different, or pairs thereof are the same, optionally bound directly to each other by a single or double formation, each one alone or together representing an aromatic ring from the group of phenyl, naphthyl, anthracyl, or phenanthryl, which may be unsubstituted or mono- or polysubstituted by C<sub>n</sub>F<sub>(2n+1-x)</sub>H<sub>x</sub>, with  $1 < n < 6$ , and  $0 < x \leq 13$ , or halogen (F, Cl, Br), or representing an aromatic heterocyclic ring from the group of pyridyl, pyrazyl or pyrimidyl, which may be unsubstituted or mono- or polysubstituted by C<sub>n</sub>F<sub>(2n+1-x)</sub>H<sub>x</sub>, with  $1 < n < 6$ , and  $0 < x \leq 13$ , or halogen (F, Cl, Br), or representing an alkyl radical (C<sub>1</sub>-C<sub>8</sub>) which may be partially or completely substituted by additional groups, preferably F, Cl, N(C<sub>n</sub>F<sub>(2n+1-x)</sub>H<sub>x</sub>)<sub>2</sub>, O(C<sub>n</sub>F<sub>(2n+1-x)</sub>H<sub>x</sub>), SO<sub>2</sub>(C<sub>n</sub>F<sub>(2n+1-x)</sub>H<sub>x</sub>), C<sub>n</sub>F<sub>(2n+1-x)</sub>H<sub>x</sub>, with  $1 < n < 6$ , and  $0 < x \leq 13$ , or wherein

15

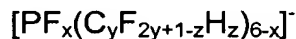
20

OR<sup>1</sup> to OR<sup>4</sup>, each one alone or together, represent an aromatic or aliphatic carboxyl, dicarboxyl, oxysulfonyl, or oxycarboxyl radical which may be partially or completely substituted by additional groups, preferably F, Cl, N(C<sub>n</sub>F<sub>(2n+1-x)</sub>H<sub>x</sub>)<sub>2</sub>, O(C<sub>n</sub>F<sub>(2n+1-x)</sub>H<sub>x</sub>), SO<sub>2</sub>(C<sub>n</sub>F<sub>(2n+1-x)</sub>H<sub>x</sub>), C<sub>n</sub>F<sub>(2n+1-x)</sub>H<sub>x</sub>, with  $1 < n < 6$ , and  $0 < x \leq 13$  (DE 100 26 565), may be included in the electrolyte. Ionic liquids K<sup>+</sup>A<sup>-</sup> wherein K<sup>+</sup> is as defined above and

25

30

A<sup>-</sup> represents an anion selected from the group of



with

35

$$1 \leq x < 6,$$

$$1 \leq y \leq 8, \text{ and}$$

$$0 \leq z \leq 2y+1,$$

may also be included (DE 100 27 995).

5 The compounds according to the invention can be used in electrolytes for electrochemical cells including an anode material which consists of coated metal cores selected from the group of Sb, Bi, Cd, In, Pb, Ga, and tin, or alloys thereof (DE 100 16 024). The process for producing such anode material is characterized in that

10

a) a suspension or sol of the metal or alloy core in urotropine is prepared,

b) the suspension is emulsified with C<sub>5</sub>-C<sub>12</sub> hydrocarbons,

c) the emulsion is precipitated on the metal or alloy core, and

15

d) the metal hydroxides or oxyhydroxides are converted to the corresponding oxides by tempering.

20

The compounds according to the invention can also be used in electrolytes for electrochemical cells with cathodes made of common lithium intercalation and insertion compounds, but also with cathode materials consisting of lithium mixed oxide particles which are coated with one or more metal oxides (DE 199 22 522) by suspending the particles in an organic solvent, adding to the suspension a solution of a hydrolyzable metal compound and a hydrolyzing solution, and subsequently filtrating,

25

drying and optionally calcining the coated particles. Said materials may also consist of lithium mixed oxide particles coated with one or more polymers (DE 199 46 066), obtained using a process wherein the particles are suspended in a solvent, and the coated particles subsequently are filtrated off, dried and optionally calcined. Likewise, the compounds

30

according to the invention can be used in systems including cathodes comprised of lithium mixed oxide particles having one or more coatings of alkali metal compounds and metal oxides (DE 100 14 884). The process for producing these materials is characterized in that the particles are suspended in an organic solvent, an alkali metal salt compound suspended

35

in an organic solvent is added, metal oxides dissolved in an organic solvent are added, the suspension is added with a hydrolyzing solution, and the coated particles subsequently are filtrated off, dried and calcined. Likewise, the compounds according to the invention can be used in systems including anode materials with doped tin oxide (DE 100 25 761). Such an

anode material is prepared by

- a) adding urea to a tin chloride solution,
- b) adding the solution with urotropine and a suitable doping compound,
- 5 c) emulsifying the sol thus obtained in petroleum ether,
- d) washing the resulting gel, and removing the solvent by suction, and
- e) drying and tempering the gel.

Likewise, the compounds according to the invention can be used in  
10 systems including anode materials with reduced tin oxide (DE 100 25 762).  
This anode material is produced by

- a) adding urea to a tin chloride solution,
- b) adding the solution with urotropine,
- 15 c) emulsifying the sol thus obtained in petroleum ether,
- d) washing the resulting gel, and removing the solvent by suction,
- e) drying and tempering the gel, and
- f) exposing the resulting  $\text{SnO}_2$  to a stream of reducing gas in a gas-  
feedable oven.

20

Preferably, the salts according to the invention are used as conducting  
salts in their pure form, because particularly good reproducibility of the  
electrochemical properties can be ensured in this way.

25 The invention is also directed to a method of producing the  
tetrakisfluoroalkylborate salts of the invention having the general formula  
(1) wherein the ligands R each are identical, representing a  $\text{CF}_3$  radical.

In this method, at least one salt of general formula (X)

30



wherein  $\text{M}^{n+}$  and n have the above-stated meanings, is fluorinated by  
reacting with at least one fluorinating agent in at least one solvent, and the  
35 fluorinated compound of general formula (I) thus obtained is purified and  
isolated according to methods well-known to those skilled in the art.

Immediately subsequent to fluorination, the tetrakisfluoroalkylborate salts  
frequently have a purity of >99%. If necessary, further purification of the

salts can be effected according to conventional methods well-known to those skilled in the art, e.g. by recrystallization in a suitable solvent or mixture of solvents. A person skilled in the art may select suitable solvents or mixtures of solvents by means of simple preliminary tests.

5

The compounds of general formula (X) can be synthesized in analogy to the method published in E. Bernhardt, G. Henkel, H. Willner, Z. Anorg. Allg. Chem. 2000, Vol. 626, p. 560. This citation is hereby incorporated by reference and is deemed to be part of the disclosure.

10

In the method according to the invention, the reaction with the fluorinating agent preferably is effected at a temperature ranging from -80 to +20°C, more preferably at a temperature ranging from -60 to 0°C

15

In the method according to the invention, it is preferred to use fluorine, chlorine fluoride, chlorine trifluoride, chlorine pentafluoride, bromine trifluoride, bromine pentafluoride, or a mixture of at least two of these fluorinating agents as suitable fluorinating agents. The use of chlorine fluoride, chlorine trifluoride or a mixture of at least two fluorinating agents containing chlorine fluoride and/or chlorine trifluoride is particularly preferred.

20

It is preferred to use hydrogen fluoride, iodine pentafluoride, dichloromethane, chloroform, or a mixture of at least two of these solvents as suitable solvent in the fluorination of the salts of general formula (X). It is particularly preferred to use hydrogen fluoride as solvent.

25

The tetrakisfluoroalkylborate salts of general formula (I) according to the invention are also suitable for use in solid electrolytes. In the meaning of the invention, solid electrolytes are understood to be polymer electrolytes normally having an optionally cross-linked polymer and a conducting salt, as well as gel electrolytes which, in addition to an optionally crosslinked polymer and a conducting salt, include at least one solvent.

30

35 The present invention therefore is also directed to a mixture including

- a) at least one tetrakisfluoroalkylborate salt of general formula (I), and
- b) at least one polymer.

Mixture in the meaning of the present invention includes pure mixtures of components a) and b), mixtures wherein the salt of component a) is included in the polymer of component b), and mixtures wherein chemical and/or physical bonds exist between the salt of component a) and the polymer of component b).

In a preferred embodiment of the present invention, the mixture of the invention includes from 5 to 90 wt.-% of component a) and from 95 to 5 wt.-% of component b), more preferably from 10 to 80 wt.-% of component a) and from 90 to 20 wt.-% of component b). Each of the specified weight ratios relates to the sum of components a) and b).

As component b), the mixture according to the invention preferably includes a homopolymer or copolymer of acrylonitrile, vinylidene difluoride, methyl methacrylate, tetrahydrofuran, ethylene oxide, siloxane, phosphazene or a mixture of at least two of the above-mentioned homopolymers and/or copolymers.

More preferably, component b) is a homopolymer or copolymer of vinylidene difluoride, acrylonitrile, methyl (meth)acrylate, tetrahydrofuran, and especially preferably a homopolymer or copolymer of vinylidene difluoride.

These homo- and copolymers of vinylidene difluoride are being marketed under the names of Kynar<sup>®</sup> and Kynarflex<sup>®</sup> by Atofina Chemicals, Inc., and under the name of Solef<sup>®</sup> by the Solvay Company.

The polymers used according to the invention may also be at least partially crosslinked. Crosslinking can be effected according to conventional methods well-known to those skilled in the art.

In addition to the tetrakisfluoroalkylborate salts of general formula (I) and the polymers, the mixture according to the invention may include a solvent or a mixture of solvents comprised of two or more solvents.

Preferred solvents are organic carbonates, preferably ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, or methyl propyl carbonate, organic esters, preferably methyl formate, ethyl formate, methyl acetate, ethyl

acetate, methyl propionate, ethyl propionate, methyl butyrate, ethyl butyrate,  $\gamma$ -butyrolactone, organic ethers, preferably diethyl ether, dimethoxyethane, diethoxyethane, organic amides, preferably dimethylformamide or dimethylacetamide, sulfur-containing solvents, preferably dimethyl sulfoxide, dimethyl sulfide, diethyl sulfide, or propanesulfone, aprotic solvents, preferably acetonitrile, acrylonitrile, or acetone, or at least partially fluorinated derivatives of the above-mentioned solvents, or mixtures of at least two of these solvents and/or fluorinated derivatives of these solvents.

10

The present invention is also directed to the use of at least one tetrakisfluoro-alkylborate salt according to the invention or of a mixture according to the invention in electrolytes, primary batteries, secondary batteries, capacitors, supercapacitors, and/or galvanic cells, optionally in combination with other well-known conducting salts and/or additives.

15

The invention is also directed to electrolytes, primary and secondary batteries, capacitors, supercapacitors, and galvanic cells including at least one tetrakisfluoroalkylborate salt according to the invention having general formula (I) or a mixture according to the invention and optionally other conducting salts and/or additives. Other conducting salts and additives are known to those skilled in the art, e.g. from Doron Auerbach, Nonaqueous Electrochemistry, Marc Dekker Inc., New York, 1999; D. Linden, Handbook of Batteries, Second Edition, McGraw-Hill Inc., New York, 1995; as well as G. Mamantov and A. I. Popov, Chemistry of Nonaqueous Solutions, Current Progress, VCH Verlagsgesellschaft, Weinheim, 1994. These citations are hereby incorporated by reference and are deemed to be part of the disclosure.

20

25

The electrolytes according to the invention preferably include concentrations of the tetrakisfluoroalkylborate salt(s) of the invention of from 0.01 to 3 mol/l, more preferably from 0.01 to 2 mol/l, with 0.1 to 1.5 mol/l being particularly preferred.

30

As solvents for the salts of the invention, the electrolytes preferably include organic carbonates, preferably ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, or methyl propyl carbonate, organic esters, preferably methyl formate, ethyl formate, methyl acetate, ethyl acetate, methyl propionate,

35

ethyl propionate, methyl butyrate, ethyl butyrate,  $\gamma$ -butyrolactone, organic ethers, preferably diethyl ether, dimethoxyethane, diethoxyethane, organic amides, preferably dimethylformamide or dimethylacetamide, sulfur-containing solvents, preferably dimethyl sulfoxide, dimethyl sulfide, diethyl sulfide, or propanesulfone, aprotic solvents, preferably acetonitrile, acrylonitrile, or acetone, or at least partially fluorinated derivatives of the above-mentioned solvents, or mixtures of at least two of these solvents and/or fluorinated derivatives of these solvents.

10 The tetrakisfluoroalkylborate salts according to the invention and the mixtures of the invention are advantageous in that signs of decomposition in the presence of water are absent or nearly absent over a long period of time, and that they have from good to very good solubility in most solvents or mixtures of solvents.

15 Furthermore, they have high thermal stability and high chemical stability both in the solid and dissolved states. Thus, the salts and mixtures according to the invention are stable, for example with respect to strong oxidants such as fluorine.

20 By virtue of these properties, electrolytes, batteries, capacitors, supercapacitors, and galvanic cells including these conducting salts can also be used under extreme conditions, such as high temperatures, with no adverse effects on their service life and performance by such conditions.

25 Furthermore, these batteries, capacitors, supercapacitors, and galvanic cells are remarkable for their highly constant voltage, unrestricted functionality over many charge- discharge cycles, as well as low production cost.

30 The use of the tetrakisfluoroalkylborate salts or mixtures according to the invention in large batteries, such as those used in electric road vehicles or hybrid road vehicles is also highly advantageous, because no toxic and strongly etching hydrogen fluoride will be formed upon damage of the batteries, e.g. in case of an accident, not even upon contact with water, e.g. humidity or fire-fighting water.

With reference to the examples, the invention will be illustrated below. These examples merely are intended to illustrate the invention and do not

limit the general idea of the invention.

## EXAMPLES

### 5 Example 1

#### Synthesis of Potassium Tetrakis(trifluoromethyl)borate, $K[B(CF_3)_4]$

##### 1a)

10

85 mg (0.60 mmol) of  $NH_4[B(CN)_4]$  was dried under vacuum in a 250 ml PFA (tetrafluoroethylene/perfluorinated propyl vinyl ether copolymer) reactor. Subsequently, about 5 ml of hydrogen fluoride and 28.4 mmol of chlorine fluoride (metered by gas-volumetric means) were condensed into the reactor. The reaction mixture was slowly heated at a temperature of from 20 to 25°C with stirring, and stirring was continued for another 48 hours at this temperature. Thereafter, all of the volatile components were removed from the reaction mixture under vacuum. The radical thus obtained was taken up in about 5 ml of distilled water, neutralized with 200 mg of potassium carbonate, and the water then was removed under vacuum. The potassium tetrakis(trifluoromethyl)borate,  $K[B(CF_3)_4]$ , was extracted with diethyl ether from the resulting radical. The diethyl ether was distilled off to yield 173 mg (0.53 mmol) of  $K[B(CF_3)_4]$ .

25 Alternatively, the synthesis of  $K[B(CF_3)_4]$  can be performed according to the protocols 1b) or 1 c):

##### 1b)

30

1.512 g (11.4 mmol) of  $NH_4[B(CN)_4]$  was dried under vacuum in a 500 ml stainless steel autoclave. Subsequently, about 30-40 ml of hydrogen fluoride and 562 mmol of chlorine fluoride (metered by gas-volumetric means) were condensed into the autoclave. The reaction mixture then was slowly heated at a temperature of from 20 to 25°C with stirring, and stirring was continued for another 48-72 hours at this temperature. Thereafter, all of the volatile components were removed from the reaction mixture under vacuum. The radical thus obtained was taken up in about 50 ml of distilled water, neutralized with 3.8 g of potassium carbonate, and the water then was removed under vacuum. The potassium tetrakis(trifluoromethyl)borate,

35

K[B(CF<sub>3</sub>)<sub>4</sub>], was extracted with diethyl ether from the resulting radical. The diethyl ether was distilled off to yield 3.4 g (11.2 mmol) of K[B(CF<sub>3</sub>)<sub>4</sub>].

1c)

5

105 mg (0.79 mmol) of NH<sub>4</sub>[B(CN)<sub>4</sub>] was dried under vacuum in a 250 ml PFA(tetrafluoroethylene/perfluorinated propyl vinyl ether copolymer) reactor. Subsequently, about 5 ml of hydrogen fluoride and 11.4 mmol of chlorine trifluoride (metered by gas-volumetric means) were condensed into the reactor. The reaction mixture then was slowly heated at a temperature of from 20 to 25°C with stirring, and stirring was continued for another 19 hours at this temperature. Thereafter, all of the volatile components were removed from the reaction mixture under vacuum. The radical thus obtained was taken up in about 7 ml of distilled water, neutralized with 300 mg of potassium carbonate, and the water then was removed under vacuum.

The potassium tetrakis(trifluoromethyl)borate, K[B(CF<sub>3</sub>)<sub>4</sub>], was extracted with diethyl ether from the resulting radical. The ether was distilled off to yield 209 mg (0.69 mmol) of K[B(CF<sub>3</sub>)<sub>4</sub>].

Part of the K[B(CF<sub>3</sub>)<sub>4</sub>] was dissolved in deuterated acetonitrile (200 mg/ml, 1 mol/25 mol CD<sub>3</sub>CN) and characterized using <sup>11</sup>B and <sup>19</sup>F NMR spectroscopy. The <sup>11</sup>B NMR spectrum was recorded at a frequency of 160.5 MHz, the <sup>19</sup>F NMR spectrum at 470.6 MHz, and the <sup>13</sup>C NMR spectrum at 125.8 MHz. As internal standard, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>OBF<sub>3</sub> with δ = 0 ppm was used in the <sup>11</sup>B NMR spectroscopy, CFCF<sub>3</sub> with δ = 0 ppm in the <sup>19</sup>F NMR spectroscopy, and CFCF<sub>3</sub> with δ = 0 ppm in the <sup>13</sup>C NMR spectroscopy. The NMR-spectroscopic data were as follows:

30

<sup>11</sup>B NMR spectrum:

δ = -18.94 ppm, <sup>2</sup>J(<sup>11</sup>B<sup>19</sup>F) = 25.92 Hz, <sup>1</sup>J(<sup>11</sup>B<sup>13</sup>C) = 73.4 Hz,  
<sup>1</sup>Δ<sup>11</sup>B(<sup>12/13</sup>C) = 0.0030 ppm at a line width of 0.5 Hz.

35

<sup>19</sup>F NMR spectrum:

δ = -61.60 ppm, <sup>2</sup>J(<sup>19</sup>F<sup>11</sup>B) = 25.92 Hz, <sup>2</sup>J(<sup>19</sup>F<sup>10</sup>B) = 8.68 Hz,  
<sup>2</sup>Δ<sup>19</sup>F(<sup>10/11</sup>B) = 0.0111 ppm, <sup>1</sup>J(<sup>19</sup>F<sup>13</sup>C) = 304.3 Hz, <sup>1</sup>Δ<sup>19</sup>F(<sup>12/13</sup>C) = 0.1315

ppm,  $^3J(^{19}\text{F}^{13}\text{C}) = 3.9$  Hz,  $^3\Delta^{19}\text{F}(^{12/13}\text{C}) = 0.0010$  ppm,  $^4J(^{19}\text{F}^{19}\text{F}) = 5.8$  Hz at a line width of 0.4 Hz.

$^{13}\text{C}$  NMR spectrum:

5

$\delta = 132.9$  ppm,  $^1J(^{13}\text{C}^{19}\text{F}) = 304.3$  Hz,  $^3J(^{13}\text{C}^{19}\text{F}) = 4.0$  Hz,  $^1J(^{13}\text{C}^{11}\text{B}) = 73.4$  Hz,  $^1J(^{13}\text{C}^{10}\text{B}) = 24.6$  Hz,  $^1\Delta^{13}\text{C}(^{10/11}\text{B}) = 0.0029$  ppm at a line width of 1.5 Hz.

- 10 The purity of the potassium tetrakis(trifluoromethyl)borate thus obtained was >99%.  $\text{K}[\text{B}(\text{CF}_3)_4]$  is readily soluble in water, diethyl ether and acetonitrile, but insoluble in dichloromethane, pentane and heptane. According to the differential scanning calorimetry measurements, the salt is stable in the solid state up to  $320^\circ\text{C}$  ( $\Delta H = -90$  J/g), having two phase transformations at  
15  $-63^\circ\text{C}$  ( $\Delta H = 4.5$  J/g) and  $-47^\circ\text{C}$  ( $\Delta H = 7.8$  J/g).

When using other carbonates or mixtures thereof instead of potassium carbonate in the neutralization of the respective crude product, e.g. lithium carbonate, sodium carbonate, rubidium carbonate, or cesium carbonate,  
20 the corresponding lithium, sodium, rubidium, or cesium tetrakis(trifluoromethyl)borate salts can be obtained in an analogous fashion, the corresponding lithium or sodium salt having solvent molecules bound therein which can be removed successively by slowly heating the respective salt.

25

## Example 2

### Synthesis of $[\text{Li}(\text{THF})_x][\text{B}(\text{CF}_3)_4]$

- 30 173 mg of  $\text{K}[\text{B}(\text{CF}_3)_4]$  (0.57 mmol) and 24 mg of lithium chloride were dried under vacuum in a 50 ml glass flask equipped with a polytetrafluoroethylene valve. Subsequently, about 10 ml of tetrahydrofuran was condensed into the flask, and the reaction mixture was stirred for one hour at a temperature of from  $20$  to  $25^\circ\text{C}$ . A precipitate of potassium  
35 chloride formed which subsequently was filtrated off. The solution thus obtained was thoroughly concentrated at a temperature of from  $20$  to  $25^\circ\text{C}$  under vacuum. Following removal of the tetrahydrofuran, 300 mg of  $[\text{Li}(\text{THF})_x][\text{B}(\text{CF}_3)_4]$  was obtained.

In its solid state, lithium tetrakis(trifluoromethyl)borate is stable up to 168°C ( $\Delta H = -260$  J/g). It is readily soluble in water, tetrahydrofuran, acetonitrile, methanol, and acetone. The tetrahydrofuran solvate molecules are removed one by one up to 140°C (97°C,  $\Delta H = 7$  g/J, 130°C,  $\Delta H = 4$  J/g).

5

#### Example 3

4.233 g (12.99 mmol) of  $K[B(CF_3)_4]$  and 1.225 g (13.07 mmol) of  $Li[BF_4]$  were added to 13.052 g of a solvent mixture of ethylene carbonate, dimethyl carbonate and diethyl carbonate at a ratio of 2:1:2. A precipitate of  $K[BF_4]$  formed which was removed by filtration. The solution of  $Li[B(CF_3)_4]$  (14.522 g, 11.7 ml) thus obtained had a salt concentration of 22.6 wt.-% or 0.96 mol/l.

#### 15 Example 4

##### Synthesis of 1-ethyl-3-methyl imidazolium tetrakis(trifluoromethyl)borate

Equimolar amounts of potassium tetrakis(trifluoromethyl)borate and 1-ethyl-3-methylimidazolium chloride were suspended in acetonitrile at a temperature of from 20 to 25°C. Subsequently, this mixture was stirred for 10 hours at this temperature and vacuum-filtrated over a glass frit with cooling so as to completely remove the potassium chloride having formed. The solvent was distilled off under vacuum, and the product thus obtained was dried under vacuum.

#### Example 5

##### Comparison of the Specific Ionic Conductance of $Li[B(CF_3)_4]$ and $LiPF_6$

30

Solutions of each salt in a mixture of ethylene carbonate, diethyl carbonate and dimethyl carbonate at a volume ratio of 2:1:2 were prepared and measured at a temperature of 25°C.

35 The conductivity measurements were carried out using a Knick 703 conductometer and a Knick 4-pole measuring cell with jacket tube. Thermostating was effected in a TI 4 conditioning cabinet, and the temperature was controlled using a Pt 100 resistance thermometer.

The respective concentrations and the respective ionic conductivities are illustrated in Table 1 below:

TABLE 1

5

	Li[B(CF <sub>3</sub> ) <sub>4</sub> ]	LiPF <sub>6</sub>
Concentration of solution [mol/l]	0.96	1
Ionic conductivity [mS/cm]	10.1	9.6

Compared to LiPF<sub>6</sub>, the Li[B(CF<sub>3</sub>)<sub>4</sub>] salt according to the invention has an improved specific ionic conductance.

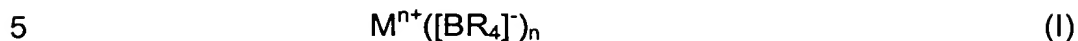
10 Example 6

Tests Relating to the Electrochemical Stability of Li[B(CF<sub>3</sub>)<sub>4</sub>]

15 In a measuring cell including platinum working electrode, lithium counterelectrode and lithium reference electrode, three consecutive cyclic voltammograms were recorded on a 0.96 molar solution of Li[B(CF<sub>3</sub>)<sub>4</sub>] in ethylene carbonate, diethyl carbonate and dimethyl carbonate (volume ratio 2:1:2). To this end, starting from the rest potential, the potential initially  
20 was increased to 6.0 V against the potential of Li/Li<sup>+</sup> at an advance rate of 10 mV/s and then lowered to return to the rest potential. The cyclic voltammograms thus obtained indicated no evidence of electrolyte decomposition.

## Claims

1. Tetrakisfluoroalkylborate salts of general formula (I)



wherein

10  $M^{n+}$  is a univalent, bivalent, or trivalent cation,  
each of the ligands R are the same and represent  $(C_xF_{2x+1})$ , with  $1 \leq x \leq 8$ ,  
and  $n = 1, 2$  or  $3$ .

- 15 2. The tetrakisfluoroalkylborate salts according to claim 1, characterized in that the  $M^{n+}$  cation is an alkali metal cation, preferably a lithium, sodium or potassium cation, and more preferably a lithium cation.

- 20 3. The tetrakisfluoroalkylborate salts according to claim 1, characterized in that the  $M^{n+}$  cation is a magnesium or aluminum cation.

- 25 4. The tetrakisfluoroalkylborate salts according to claim 1, characterized in that  $M^{n+}$  is an organic cation, preferably a nitrosyl cation, a nitril cation, or an organic cation of general formula  $[N(R^7)_4]^+$ ,  $[P(R^7)_4]^+$ ,  $[P(N(R^7)_2)_4]^+$ , or  $[C(N(R^7)_2)_3]^+$ , wherein each of the radicals  $R^7$  are the same or different, representing

H,

$C_oF_{2o+1-p-q}H_pA_q$ ,

or

30 A, wherein

$1 \leq o \leq 10$ ,

$0 \leq p \leq 2o+1$ ,

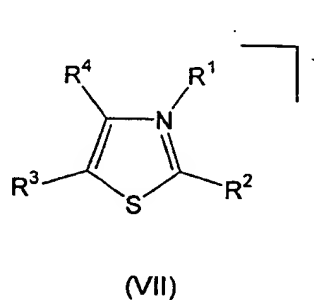
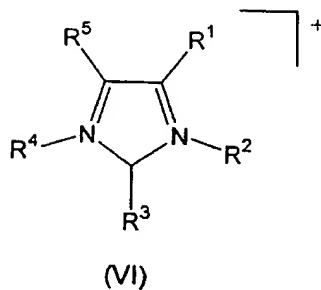
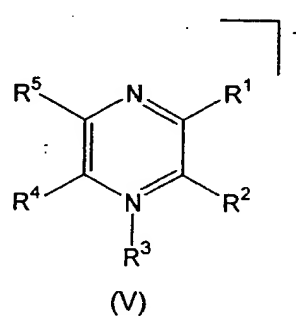
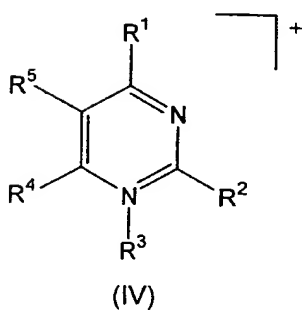
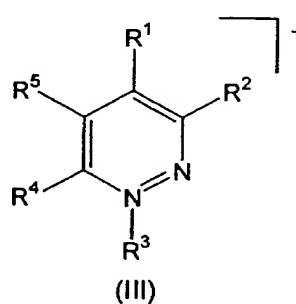
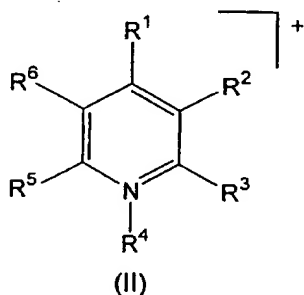
$0 \leq q \leq 2o+1$ , and

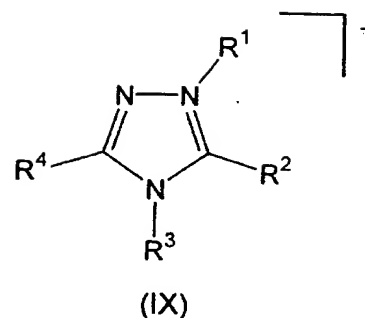
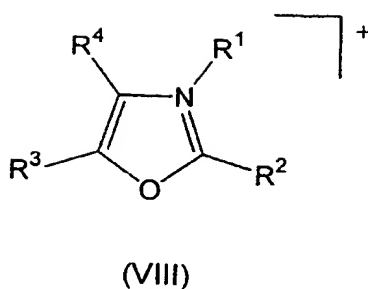
35 A represents an aromatic radical optionally having heteroatoms, or a preferably 5- or 6-membered cycloalkyl radical.

5. The tetrakisfluoroalkylborate salts according to claim 4, characterized in that  $1 \leq o \leq 6$ ,  $0 \leq p \leq 2o+1$ , and  $0 \leq q \leq 2o+1$ , and

A represents an aromatic radical optionally having heteroatoms, or a preferably 5- or 6-membered cycloalkyl radical.

6. The tetrakisfluoralkylborate salts according to claim 4 or 5, characterized in that A represents a 5- or 6-membered aromatic radical optionally including nitrogen and/or sulfur and/or oxygen atoms, or a preferably 5- or 6-membered cycloalkyl radical, preferably a phenyl or pyridine radical.
- 10 7. The tetrakisfluoroalkylborate salts according to claim 1, characterized in that  $M^{n+}$  is a heteroaromatic cation of general formulae (II) to (IX)





wherein the radicals  $R^1$  to  $R^6$ , each of which same or different, and optionally two of the radicals  $R^1$  to  $R^6$  together, represent an H, a halogen, preferably fluorine, or a  $C_{1-8}$  alkyl radical optionally substituted by F, Cl,  $N(C_aF_{(2a+1-b)}H_b)_2$ ,  $O(C_aF_{(2a-1-b)}H_b)$ ,  $SO_2(C_aF_{(2a+1-b)}H_b)$ , or  $C_aF_{(2a-1-b)}H_b$  wherein  $1 \leq a \leq 6$ , and  $0 \leq b \leq 13$ .

8. The tetrakisfluoroalkylborate salts according to any of claims 1 to 7, characterized in that each of the ligands R are the same, representing  $(C_xF_{2x+1})$ , with  $x = 1$  or 2.
9. The tetrakisfluoroalkylborate salts according to any of claims 1 to 8, characterized in that each of the ligands R are the same, representing a  $CF_3$  radical.
10. A method of producing the tetrakisfluoroalkylborate salts of claim 9, characterized in that at least one compound of general formula (X)  $M^{n+}([B(CN)_4]^-)_n$  (X) wherein  $M^{n+}$  and n have the meanings as in claims 1 to 9, is fluorinated by reacting with at least one fluorinating agent in at least one solvent, and the thus-obtained fluorinated compound according to claim 1 having the general formula (I) is purified and isolated according to usual methods.
11. The method according to claim 10, characterized in that the reaction with the fluorinating agent is performed at a temperature ranging from  $-80$  to  $+20^\circ C$ , preferably from  $-60$  to  $0^\circ C$ .
12. The method according to claim 10 or 11, characterized in that fluorine, chlorine fluoride, chlorine trifluoride, chlorine pentafluoride, bromine trifluoride, bromine pentafluoride, or a mixture of at least

two of these fluorinating agents, preferably chlorine fluoride or chlorine trifluoride or a mixture of at least two fluorinating agents containing chlorine fluoride and/or chlorine trifluoride is used as fluorinating agent.

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13. The method according to any of claims 10 to 12, characterized in that hydrogen fluoride, iodine pentafluoride, dichloromethane, chloroform, or a mixture of at least two of these solvents, preferably hydrogen fluoride, is used as solvent.

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14. A mixture, including  
a) at least one tetrakisfluoroalkylborate salt of general formula (I) according to claims 1 to 9, and  
b) at least one polymer.

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15. The mixture according to claim 14, characterized in that the mixture includes from 5 to 90 wt.-% of component a) and from 95 to 5 wt.-% of component b), preferably from 10 to 80 wt.-% of component a) and from 90 to 20 wt.-% of component b), each time relative to the sum of components a) and b).

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16. The mixture according to claim 14 or 15, characterized in that component b) is a homopolymer or copolymer of acrylonitrile, vinylidene difluoride, methyl methacrylate, tetrahydrofuran, ethylene oxide, siloxane, phosphazene or a mixture of at least two of the above-mentioned homopolymers and/or copolymers.

25

17. The mixture according to claim 16, characterized in that component b) is a homopolymer or copolymer of vinylidene difluoride, acrylonitrile, methyl methacrylate, tetrahydrofuran, and preferably a homopolymer or copolymer of vinylidene difluoride.

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18. The mixture according to any of claims 14 to 17, characterized in that the polymer is at least partially crosslinked.

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19. The mixture according to any of claims 14 to 18, characterized in that the mixture additionally includes at least one solvent.

20. The mixture according to claim 19, characterized in that organic

- carbonates, preferably ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, or methyl propyl carbonate, organic esters, preferably methyl formate, ethyl formate, methyl acetate, ethyl acetate, methyl propionate, ethyl propionate, methyl butyrate, ethyl butyrate,  $\gamma$ -butyrolactone, organic ethers, preferably diethyl ether, dimethoxyethane, diethoxyethane, organic amides, preferably dimethylformamide or dimethylacetamide, sulfur-containing solvents, preferably dimethyl sulfoxide, dimethyl sulfide, diethyl sulfide, or propanesulfone, aprotic solvents, preferably acetonitrile, acrylonitrile, or acetone, or at least partially fluorinated derivatives of the above-mentioned solvents, or mixtures of at least two of these solvents and/or fluorinated derivatives of these solvents are present as solvents.
21. Use of at least one tetrakisfluoroalkylborate salt according to any of claims 1 to 9 or at least one mixture according to any of claims 14 to 20 in electrolytes, primary batteries, secondary batteries, capacitors, supercapacitors, or galvanic cells, optionally in combination with other conducting salts and/or additives.
22. Electrolytes, including at least one tetrakisfluoroalkylborate salt according to any of claims 1 to 9 or at least one mixture according to any of claims 14 to 20.
23. The electrolytes according to claim 22, characterized in that the concentration of the tetrakisfluoroalkylborate salt(s) in the electrolyte is from 0.01 to 3 mol/l, preferably from 0.01 to 2 mol/l, and more preferably from 0.1 to 1.5 mol/l.
24. Primary batteries, including at least one tetrakisfluoroalkylborate salt according to any of claims 1 to 9 or at least one mixture according to any of claims 14 to 20.
25. Secondary batteries, including at least one tetrakisfluoroalkylborate salt according to any of claims 1 to 9 or at least one mixture according to any of claims 14 to 20.
26. Capacitors, including at least one tetrakisfluoroalkylborate salt

according to any of claims 1 to 9 or at least one mixture according to any of claims 14 to 20.

5        27.    Supercapacitors, including at least one tetrakisfluoroalkylborate salt according to any of claims 1 to 9 or at least one mixture according to any of claims 14 to 20.

10       28.    Galvanic cells, including at least one tetrakisfluoroalkylborate salt according to any of claims 1 to 9 or at least one mixture according to any of claims 14 to 20.

**Abstract**

The present invention relates to tetrakisfluoroalkylborate salts, methods of producing same, and their use in electrolytes, batteries, capacitors, supercapacitors, and galvanic cells.